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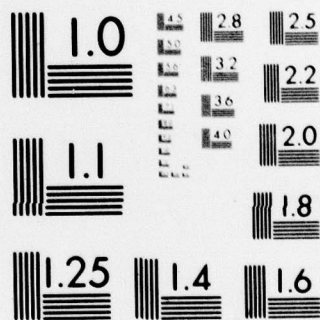
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 9	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Preparation and Photoelectronic Properties of n-type Cd_2GeO_4		5. TYPE OF REPORT & PERIOD COVERED Technical rept.
7. AUTHOR(s) Aaron Wold		6. PERFORMING ORG. REPORT NUMBER 9
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Brown University Providence, Rhode Island 02912		8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0387
11. CONTROLLING OFFICE NAME AND ADDRESS Dr. David Nelson, Code 472 Office of Naval Research Arlington, Virginia		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-359-653
12. REPORT DATE 11/1/79		13. NUMBER OF PAGES 10
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 11 Nov 79 13 13		15. SECURITY CLASS. (of this report)
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE		
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) 10 V. S. /Nguyen, S. N. /Subbarao, R. /Kershaw, K. /Dwight Aaron /Wold		
18. SUPPLEMENTARY NOTES Submitted to Materials Research Bulletin		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Photoelectrolysis Band gap Flat band potential Stability		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Cd_2GeO_4 crystallizes with an orthorhombic structure space group Pbnm (a=5.20, b=11.14, c=6.57A) as determined by the onset of photocurrent, the flat band potential is -0.80(5)V vs SCE. An indirect band gap at 3.15(5) eV and a direct band gap at 4.15(5) eV were ascertained from measurement of the photoelectronic quantum efficiency. Despite some initial loss in the photo-response during the first hour of irradiation at 1.0 W/cm ² , Cd_2GeO_4 has been shown to be far more stable as an electrode than Cd_2SnO_4 .		

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Technical Report Number 9

PREPARATION AND PHOTOELECTRONIC PROPERTIES OF n-TYPE Cd_2GeO_4

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November 1, 1979

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ABSTRACT:

Cd_2GeO_4 crystallizes with an orthorhombic structure space group Pbnm ($a = 5.20$, $b = 11.14$, $c = 6.57\text{\AA}$) as determined by the onset of photocurrent, the flat band potential is $-0.80(5)\text{V}$ vs SCE. An indirect band gap at $3.15(5)\text{ eV}$ and a direct band gap at $4.15(5)\text{ eV}$ were ascertained from measurement of the photoelectronic quantum efficiency. Despite some initial loss in the photogresponse during the first hour of irradiation at 1.0 W/cm^2 , Cd_2GeO_4 has been shown to be far more stable as an electrode than Cd_2SnO_4 .

Introduction

Transition metal oxides which have been investigated as photoanodes have been reported to have low electron mobility (of the order of $0.1\text{ cm}^2/\text{V sec}$ or less) and high carrier concentration ($\geq 10^{19}/\text{cm}^3$). In general, these oxides are made conducting by the creation of two valence states of the same transition metal and the conduction takes place by means of a hopping mechanism. Examples of such low mobility oxide semiconductors are TiO_{2-x} and WO_{3-x} (1,2). On the other hand, antimony doped tin (IV) oxide is an example of a conducting compound having few carriers with relatively high mobility (3). Another n-type semiconductor is CdO which has a band gap of 2.2 eV and a flat-band potential of -0.2V relative to a saturated calomel electrode (SCE) measured at a pH of $13.3(4)$. Cd_2SnO_4 is a ternary oxide which has been reported to show a high conductivity caused by relatively few carriers with high mobility (5). However, Cd_2SnO_4 is not stable as an anode in aqueous solutions (6). Whereas, the preparation, structure and conductivity of Cd_2GeO_4 have been reported (7), its stability and photoresponse as an anode in aqueous solutions have not

been determined. It might be expected that the substitution of germanium for tin in the ternary oxide would influence the strength of the bonding and hence the stability of the photoanode.

Synthesis

Cd_2GeO_4 was prepared by the solid state reaction of GeO_2 (Johnson Matthey, spec. pure) and CdO (obtained from the decomposition of CdCO_3). The cadmium carbonate was obtained by dissolving sufficient cadmium metal in concentrated nitric acid to give a 1M solution with respect to cadmium. Sufficient ammonium carbonate was added so that its final concentration was 1.5M. The pH of the solution was then adjusted to 10 and heated on a steam bath in order to precipitate the cadmium carbonate. The composition of cadmium carbonate was confirmed by titration of the cadmium with potassium bromate(8). Cadmium carbonate was also subjected to thermogravimetric analysis and the weight of cadmium obtained from the thermal decomposition at 825°C agreed with the calculated value.

Appropriate weights of GeO_2 and CdO were mixed and ground thoroughly. The resulting mixture was heated in an evacuated silica tube at 800°C for a total of 144 hours. The sample was removed from the furnace twice during the heat treatment and reground thoroughly. Complete reaction was confirmed by x-ray analysis using a Phillips Norelco Diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.5405\text{\AA}$) at a scan rate of $0.5\ 2\theta\ \text{min}^{-1}$.

Disks, formed by pressing aliquots of approximately 200 mg at 60,000 p.s.i., were heated in an evacuated sealed silica tube at 800°C for 72 hours. Well-sintered disks, almost white in color, were obtained by this method.

Photoelectronic Properties

The resistivity measurements were performed on several Cd_2GeO_4 disks using the van der Pauw method (9). Indium electrical contacts were applied to each disk by ultrasonic soldering. The room temperature resistivity for these disks was $0.20(2)\ \Omega\text{-cm}$. Seebeck and dc Hall measurements showed the disks to be n-type semiconductors with a carrier concentration $n = 1.05(5) \times 10^{18}/\text{cm}^3$ and a mobility $\mu = 30(3)\ \text{cm}^2/\text{V sec}$.

Electrodes were fabricated and photoelectrolysis measurements were carried out as described previously (10) using a 150 Watt xenon lamp, a monochromator (Oriel Model 7240), a glass cell with a quartz window, and a current amplifier. The electrolyte, 0.2 M sodium acetate adjusted to a pH ~ 13 with sodium hydroxide, was purged of oxygen by continuous bubbling of 85% Argon - 15% hydrogen gas.

Results and Discussion

Tarte (11) showed that Cd_2GeO_4 crystallizes with an orthorhombic structure, space group Pbnm ($a_0 = 5.20$, $b_0 = 11.13$ and $c_0 = 6.57$ Å). The cell dimensions obtained for the Cd_2GeO_4 samples reported in this paper ($a = 5.20$, $b = 11.14$, $c = 6.57$) confirm the parameters reported by Tarte.

Fig. 1 shows the photoresponse obtained with "white" xenon arc irradiation of 1.0 W/cm^2 as a function of the anode potential. As determined by the onset of photocurrent, the flat band potential is $-0.80(5) \text{ V vs SCE}$.

The spectral response measured at an anode potential of -0.2 V vs SCE is shown in Fig. 2. The quantum efficiency was obtained by dividing the observed photocurrent by the light flux incident on the cell as measured with a calibrated silicon photodiode (United Detector Technology). These results can be analyzed to determine not only the lowest optical band gap, but higher lying gaps as well (2). They yield an indirect band gap at $3.15(5) \text{ eV}$ with a band tail extending below 2.4 eV . However, no significant photocurrent is observed until a direct band gap is reached at $4.15(5) \text{ eV}$. The presence of a second direct gap above 4.5 eV is also indicated, but at this energy the quantum efficiency is sufficiently great to preclude rigorous application of the model (2). That Cd_2GeO_4 should possess a higher band gap than CdO is consistent with its flat-band potential being more negative (12).

The variation of relative photocurrent with time is shown in Fig. 3. Despite the loss of 25% of the photoresponse during the first hour of irradiation at 1.0 W/cm^2 , this curve represents good stability for a cadmium compound.

FIG. 1
Photoresponse under "white"
xenon arc irradiation of 1.0 W/cm
in $\text{pH} \approx 13$ electrolyte.

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FIG. 2
Quantum efficiency measured at an
anode potential of -0.2 V vs SCE
in $\text{pH} \approx 13$ electrolyte.

For example, Cd_2SnO_4 which crystallizes with the orthorhombic space group Pbam was found to deteriorate so rapidly that photoelectronic measurements were unreliable (6). The improved stability observed for Cd_2GeO_4 may be due to the structural difference resulting from the smaller size of Ge(IV) vs Sn(IV) . This effect may also be the origin of the observed changes in optical band gap and flat-band potential.

Acknowledgements

The Office of Naval Research, Arlington, Virginia supported the work of S. N. Subbarao and K. Dwight. Acknowledgement is made to the Solar Energy Research Institute, Golden, Colorado for the support of V. S. Nguyen. In addition, the authors would like to acknowledge the support of the Materials Research Laboratory Program at Brown University.

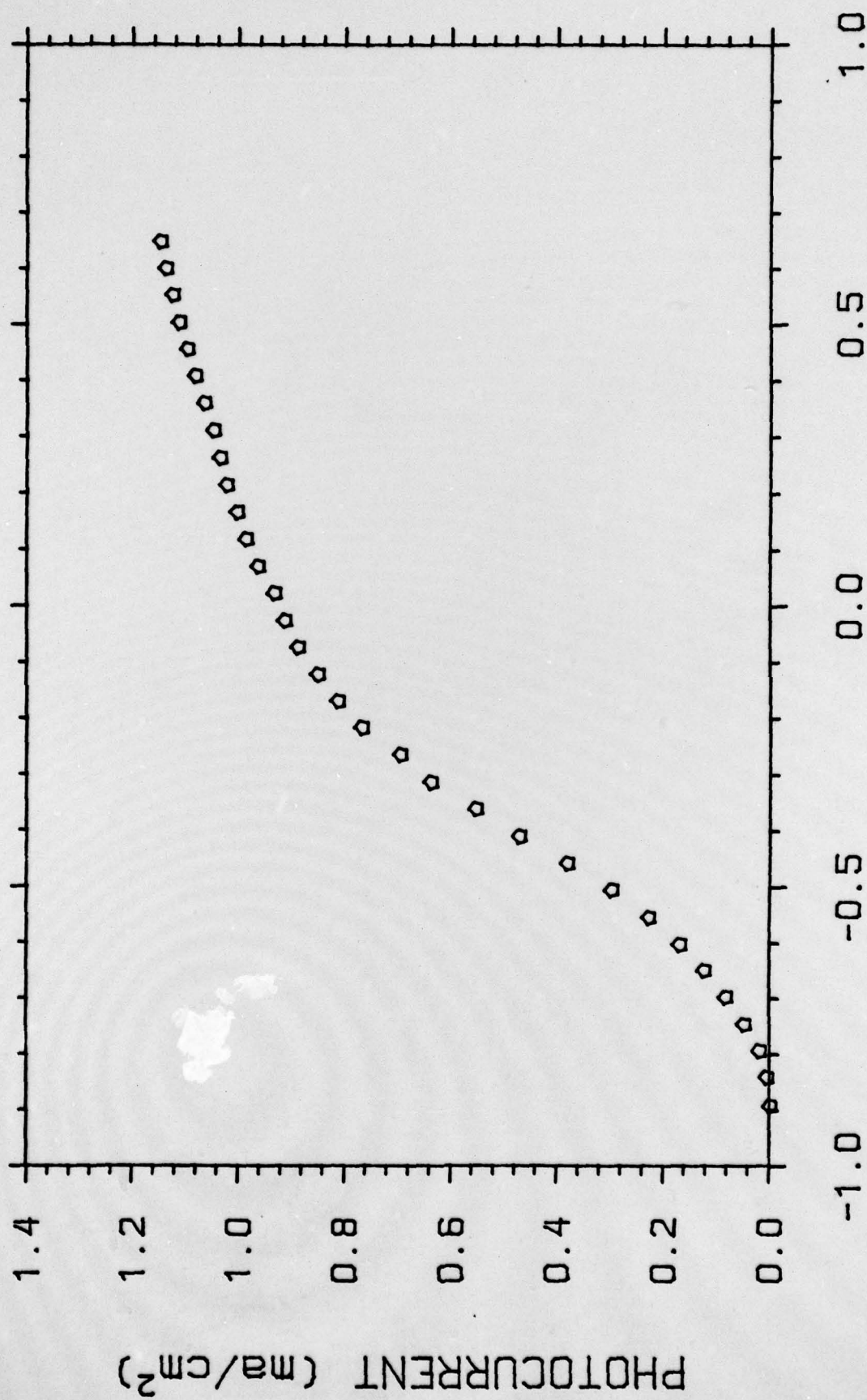
FIG. 3
Stability under "white" xenon arc irradiation of 1.0 W/cm^2 in 0.2 M sodium acetate adjusted to $\text{pH} \approx 13$.

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Cd_2GeO_4



ANODE POTENTIAL vs SCE (volts)

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Cd_2GeO_4

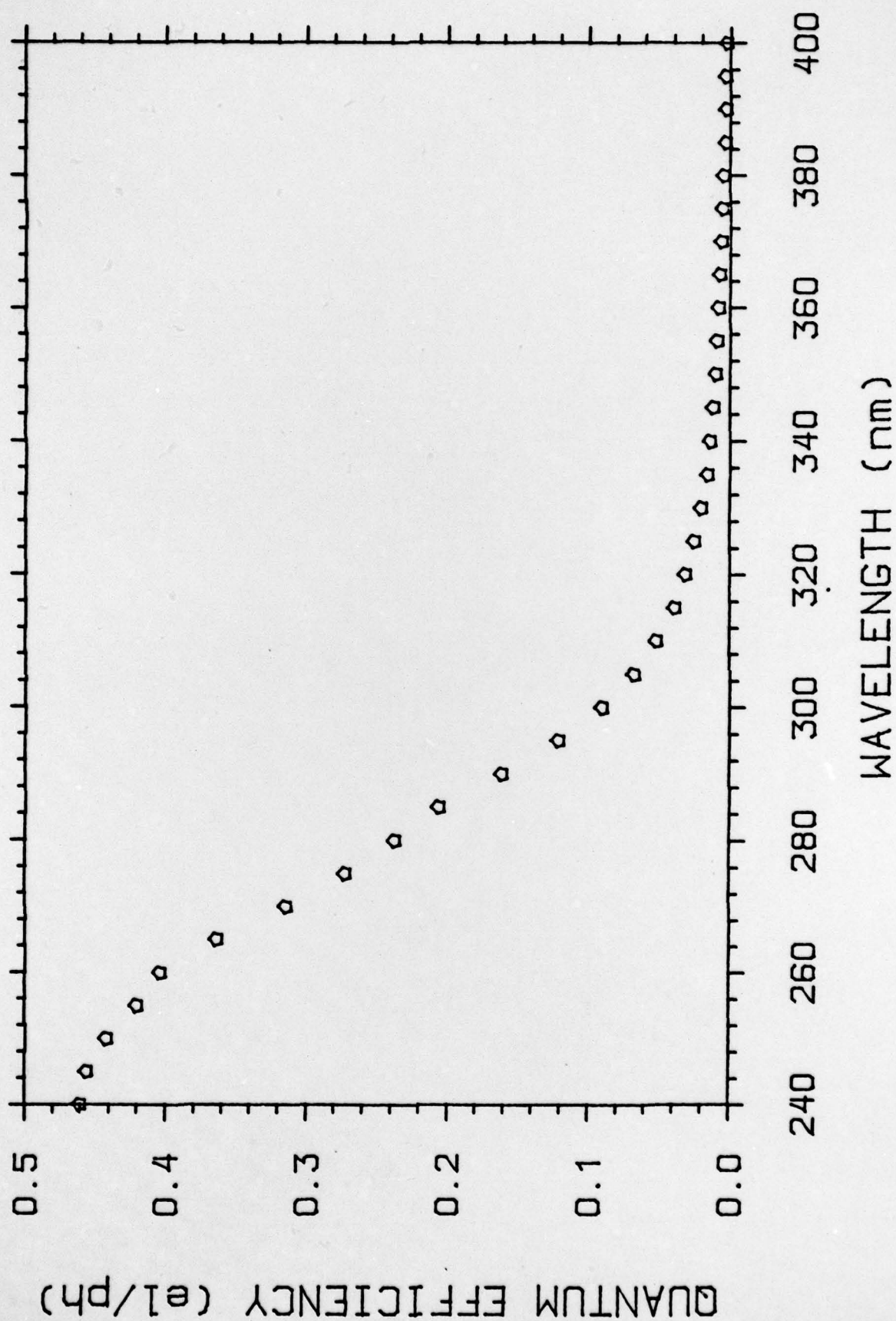
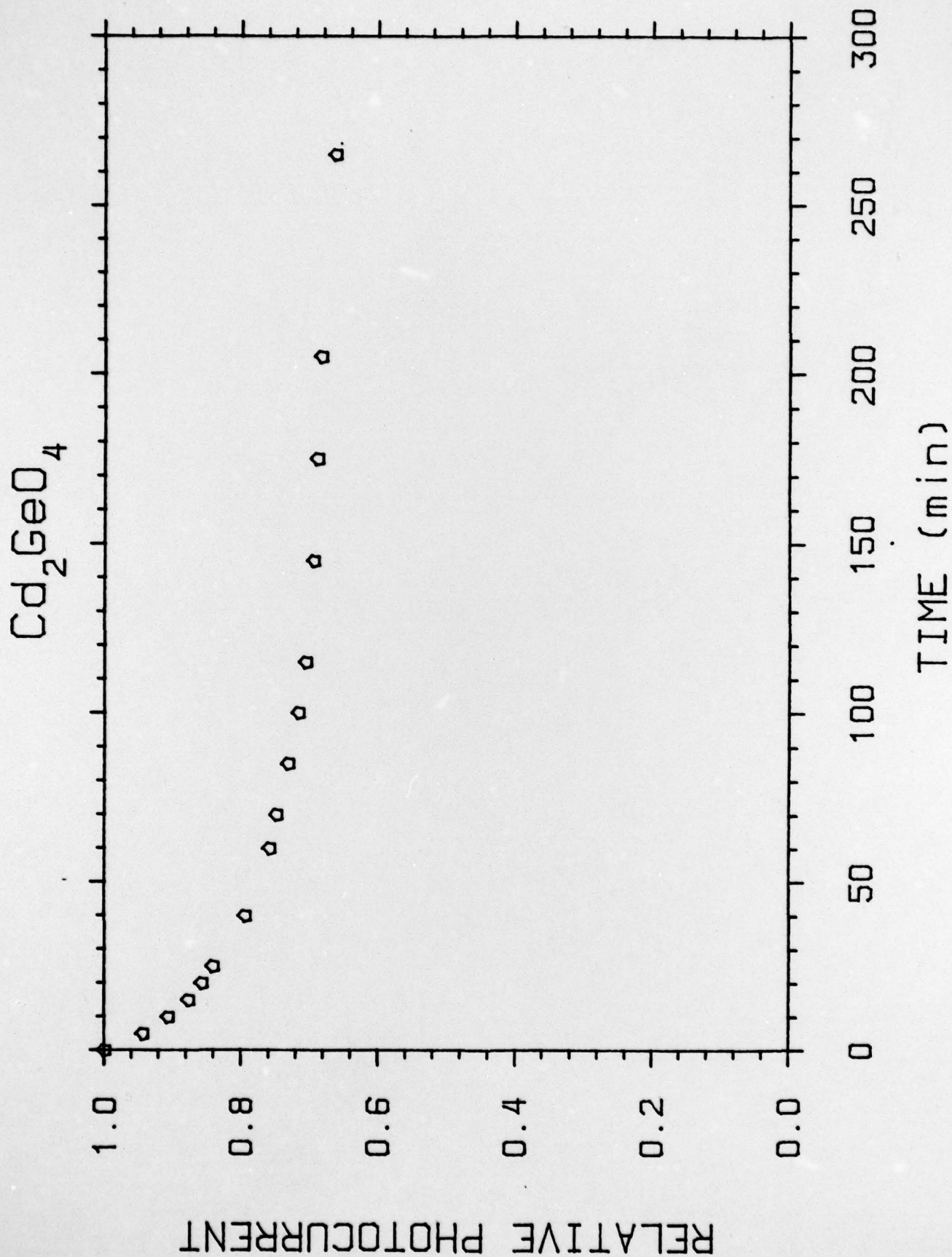


Fig 2

FIG 3



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